B41A-0034
see also B41A-0033

Micron-scale Chemical Speciation of Late Albian, Well-Preserved Fossil Samples from Tlayúa, the Mexican Solenhofen

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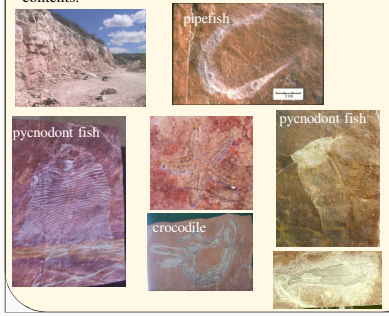
Tlayua: A site of extraordinary fossil preservation

The Tlayúa slurry is the most important paleontological locality on the American continent. A great diversity of well-preserved marine and terrestrial fossils have been found, with ages >115 million yrs. Paleomagnetic and biostratigraphic determinations in amonites and belemnites date the formation of the Tlayúa slurry to the late Albian. Fish, reptiles, invertebrates, and vegetables fossil specimens have been found to date to the Mesozoic Era. Over the past 20 yrs, >5000 specimens of >200 species have been collected in the Tepexi del Rio region,

One of the most accepted hypothesis for explaining Tlayúa's formation relies on the deposition of sediments and fauna on a shallow platform of a tropical sea. The exceptional specimen preservation found in Tlayúa has been attributed to restricted circulation of water resulting in an anaerobic and/or hypersaline environment, coupled with the general absence of infaunal species. There were periods when the site supported a rich planktonic community, resulting in the production of large quantities of calcareous ooze, causing rapid burial. The presence of diagnostic terrestrial and freshwater organisms, including arachnids, insects, lizards, and chelonians, along with typical marine fauna, suggests that Tlayúa lagoon had periodic freshwater inflow, in addition to the strong marine, lagoonal, and reefal influence. Also, some fishes from Tlayua have been found to have affinities with recent families known to inhabit brackish and freshwater environments. Some of these fish preserve gut contents.



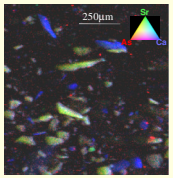
Questions

1. What happens to fossils since burial?
2. What's left of the original chemical state?

Experiments

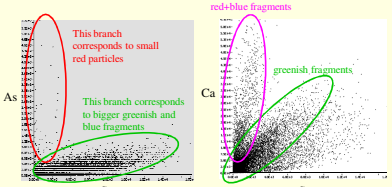
Samples of fossil fish-bone (Pachyrhizodontidae) were examined by synchrotron micro X-ray fluorescence (μXRF), micro X-ray diffraction (μXRD) and micro X-ray absorption spectroscopy (μXAS) at the Ca and As edges. The major minerals were identified by μXRD and Ca-edge μXANES. The chemistry of trace As found in the bones was examined by μXAS.

μX-ray fluorescence map



Map is 2mm square, 10μm pixels, 50ms dwell, 16keV incident. Incident beam is 16x7μm.

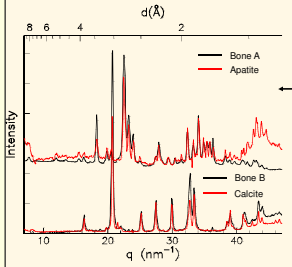
Each pixel here is colored with an amount of red corresponding to the counts in the As channel, green for Sr, and blue for Ca. The colors therefore indicate composition.



These scatterplots show the relative counts in Ca, As and Sr channels in each pixel of the map to the left. The distinct populations of points correspond to sets of particles of distinct color in the map.

The Sr/Ca ratio is ~1 wt. % for the high-Sr branch (greenish in map) and ~0.2 wt. % for the low-Sr branch (red and blue). The As/Ca ratio is ~4% for the small red particles, and 0.2 wt. % for the blue and green ones. These figures are very approximate.

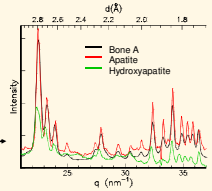
μX-ray diffraction: What are the dominant minerals?



Bone A is a Sr-rich spot and representative of a group of apatite-dominant particles.

Bone B is one of more (Sr,As)-poor particles. Both the small red ones in the μXRF map and the big blue ones are calcite-rich.

Ca μXANES confirms ID as mixture of calcite and apatite, and that apatite is well-crystallized.



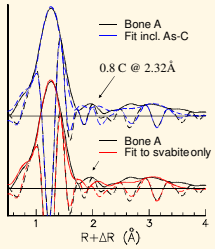
Although fresh bone is made of hydroxyapatite, this material is apatite. It must have changed over time. One particle is intermediate between apatite and hydroxyapatite, supporting the idea of a transformation.

The bone particles are either apatite or calcite. For another example of replacement by calcite, see poster B41A-0033

Note: AsO_4^{3-} can substitute for PO_4^{3-} in apatite, and Sr can substitute for Ca in both calcite and apatite. This may explain why apatite-rich particles also show lots of Sr, As. This does NOT explain why there are As-rich calcite particles.

As μX-ray spectroscopy: Where's the arsenic?

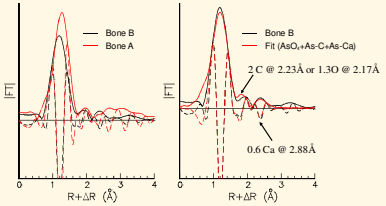
Apatite-rich particles (2 measured)



Svabite is apatite with PO_4^{3-} replaced by AsO_4^{3-}. The lower fit is to the svabite structure with adjustments for 1NN and higher distances, amplitudes and $\Delta\sigma^2$, for 7 parameters. The upper fit adds an As→C shell to describe the peak at 2Å (indicated).

These particles seem to be As-substituted apatite with perhaps some organo-As.

Calcite, As-rich particles (2 measured)



Comparing with apatite-rich bone (bone A), we find more disorder in the AsO_4 tetrahedron and a shell which might be As→C, similar to that in bone A. The spectrum is consistent with an organic and a short As-Ca distance and doesn't match literature on As-sorbed calcite.

Conclusions

1. The bone composition changed inhomogeneously, into apatite and calcite.
2. As and Sr was absorbed into the bone, with As substituting into apatite and maybe forming organo-As complexes.
3. As is mostly in the 5+ state in all of 4 spots tested.
4. In calcite-rich fragments, As is not simply sorbed on calcite.

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